

Rec'd PCT/PTRA 15 OCT 2004

## PATENT COOPERATION TREATY

PCT

RECEIVED

02 AUG 2004

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P24157PC00	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/ZA 03/00052	International filing date (day/month/year) 15.04.2003	Priority date (day/month/year) 16.04.2002
International Patent Classification (IPC) or both national classification and IPC C10G2/00		
Applicant SASOL TECHNOLOGY (PROPRIETARY) LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
  
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
  - This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 9 sheets.
  
3. This report contains indications relating to the following items:
  - I  Basis of the opinion
  - II  Priority
  - III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV  Lack of unity of invention
  - V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI  Certain documents cited
  - VII  Certain defects in the international application
  - VIII  Certain observations on the international application

Date of submission of the demand 15.10.2003	Date of completion of this report 30.07.2004
Name and mailing address of the International preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Rumbo, A Telephone No. +49 89 2399-8407



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/ZA 03/00052

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-3, 7-14, 17-19	as originally filed
4, 5, 6, 15, 16, 20	received on 10.03.2004 with letter of 10.03.2004

**Claims, Numbers**

1-11	received on 10.03.2004 with letter of 10.03.2004
------	--

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/ZA 03/00052

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1-9,11
	No:	Claims	10
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/ZA 03/00052

SECTION V (NOVELTY AND INVENTIVE STEP)

1. The application does not meet the requirements of Article 34(2)b PCT.

The introduction of the term "metal" in the claims and the description extends the claimed subject-matter beyond that originally filed. The only supported terms in the application originally filed are alkali, alkali oxide, K, Na, K<sub>2</sub>O and Na<sub>2</sub>O. Only those terms can be explicitly used in order to modify the claims. Terms which are not explicitly cited in the application originally filed cannot be introduced within the description or the claims.

2. The subject-matter of claim 10 (PRODUCT) does not meet the requirements of Article 33(2) PCT. The wording of product claim 10 concerns any kind of hydrocarbon (for instance butane, naphtha, propane ethane) which could have been obtained by any one of the processes disclosed in the process claims 1 to 9. Evidently none of the hydrocarbons cited above or any other obtained via a FT synthesis can be considered novel per se (see also D1=US-A- 4 361 503 wherein the explicit products are cited at table 3). In the absence of a differentiating technical feature explicitly included within the wording of the product claim its novelty cannot be acknowledged (Article 33(2) PCT). Nowhere in the application originally filed such a differentiating technical feature for a product can be found, in view of the products disclosed in D1, and consequently the product claim should be deleted since it does not meet the requirements of novelty.

3. The subject-matter of claim 1-9 (process) and 11 (use) meets the requirements of Article 33(2) PCT.

3.1 D1 (see col. 3, lines 55-68) explicitly refers back to the catalyst to be used in the process disclosed therein is basically as being that of D2 (US-A-4 304 871 is a family member of the "application serial no. 793015 and serial no. 793016 described supra" cited explicitly at lines 60-62 of col. 3 and related thereto at lines 34-43 of col. 2) as far as the Fe(K) catalyst is concerned and differing therefrom in that a different zeolite is used (see in particular the sentence of col. 3, lines 64-68). Only example 2 of D1 contains a reference to a K poisoned zeolite as the zeolite not to be used (see col. 8, lines 57-68) but the rest therefrom (examples 1 and 3 to 5; table 3) do not contain any further potassium (K).

3.2 Provided that (see letter dated 25.05.04 point 1.2) the intended meaning of alkali concerns the amounts of K and Na (and not the contents of K<sub>2</sub>O and Na<sub>2</sub>O), it is evident that there is at least one differentiating technical feature present in the wording of the claimed subject-matter namely the presence of less than 0.02 mole K and Na instead of the 0.025 mole K present in the process disclosed in D1(+D2).

On the contrary, the H<sub>2</sub>/carbon oxide ratio > 2 cannot be accepted as a differentiating technical feature as far as the document D1 explicitly concerns ranges from 0.5 up to 6.

The teaching of D1 is therefore applicable in the whole range without exclusions

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/ZA 03/00052

**due to the presence of preferred narrower** ranges, contrary to the applicants opinion (see letter dated 25.05.04 point 2.4. page 5, lines 3-9). The claimed subject-matter meets therefore the requirements of novelty of Article 33(2) PCT.

4. The claimed subject-matter does not meet the requirements of Article 33(3)PCT.

4.1 The application originally filed does not contain any evidence that only changing the amount of K contained in a Fe catalyst (and maintaining the rest of the technical features constant) from 0.025 mole K/100g of Fe (concentration in D1(+D2)) down to 0.02 mole K/100 g Fe any kind of improvement can be achieved.

Nowhere in the application, D1 or the rest of the prior art it is proved that less than 30% C<sub>5</sub>+ on a mass basis is obtained by merely reducing the K mole content by 0.005 Mole of K/100 g. Fe. On the contrary, the IPEA considers quite unfeasible that the 53%w. C<sub>5</sub>+ obtained in example 1 respectively 56%w (ex.3), 61%w (ex.4) and 54%w (ex.5) of D1 could be reduced down to less than 30%w. by merely reducing by 0.005 mole K /100 g. Fe (from 0.025 to 0.020) the K content of the catalyst.

4.2 Concerning the "H<sub>2</sub> / carbon oxide ratio" argument provided by the applicant at page 6, lines 12-15 of the letter dated 25.05.04, the IPEA considers that no plausible grounds can be found how to reduce the obtained amounts of cut C<sub>5</sub>+ ranging from 53%w up to 61%w down to less than 30 % w. merely by increasing the H<sub>2</sub> to carbon oxide ratio from 2 to 2.05 or 2.1.

4.3 In fact the purported reduction of C5+ cut down to 30%w has only been obtained in the very particular conditions of run 5 with catalyst PSO2 Na 0.0045 and H<sub>2</sub>/(CO+CO<sub>2</sub>)=5.8 (see application originally filed page 20) which unfortunately cannot be extrapolated to any other Na or K content ranging up to 0.020 or any other H<sub>2</sub>/(CO+CO<sub>2</sub>)ratio higher than 2 (see runs 1 to 4 and 6 to 10 as well as lines 5 to 8 of page 20 of the application).

**4.4 In the absence of the evidence that a technical feature present in the wording of the independent claim is responsible for the solution of a technical problem which could not have been solved by the technical features of the prior art the inventive step of the claimed subject-matter cannot be acknowledged. In fact modifications of the prior art which do not solve a technical problem can be considered evident and therefore not inventive.**

DT05 Rec'd PCT/PTO 15 OCT 2004

ART 34 AMDT

4

a heavier hydrocarbon product despite the low alkali level. It is well-known that a high H<sub>2</sub> : CO ratio in the feed favours products which are not desirable for gasoline production. Accordingly if a low level of alkali promoter is considered a relatively low H<sub>2</sub> : CO ratio in the feed will be considered to avoid production of excessively light hydrocarbons.

Surprisingly it has now been found that if hydrocarbon synthesis of syngas is carried out in the presence of a hydrocarbon synthesis catalyst and an acidic catalyst under conditions where:

- 10 i) the hydrocarbon synthesis catalyst includes a low level of alkali metal; and  
ii) the hydrogen to carbon monoxide ratio of the syngas feed stream is relatively high,

a hydrocarbon product is produced that is suitable for use as gasoline. This is true even if the synthesis is carried out under high temperature Fischer-Tropsch conditions.

#### Disclosure of the Invention

According to the present invention there is provided a hydrocarbon synthesis process comprising the conversion of a feed of H<sub>2</sub> and at least one carbon oxide to hydrocarbons containing at least 30% on a mass basis hydrocarbons with five or more carbon atoms (hereinafter referred to as C<sub>5+</sub> compounds), the conversion being carried out in the presence of an alkali-promoted iron hydrocarbon synthesis catalyst and an acidic catalyst suitable for converting

AFT 34 AMDT

5

hydrocarbons; and the process being characterised therein that the reaction mixture formed during the conversion contains less than 0.02 mol alkali metal per 100g iron and that the H<sub>2</sub> : carbon oxide molar ratio in the feed of H<sub>2</sub> and carbon oxide is at least 2.

5

The synthesised hydrocarbons preferably contain, on a mass basis, at least 35%, more preferably at least 40% and most preferably at least 50%, C<sub>6</sub><sup>+</sup> compounds. Preferably, the process is for producing liquid fuel, especially gasoline and preferably unleaded gasoline. The process may also be used for producing hydrocarbons rich in aromatics such as benzene, toluene and xylenes and/or hydrocarbons rich in branched hydrocarbons and/or rich in olefins.

The hydrocarbon synthesis process may comprise a Fischer-Tropsch process, preferably a high temperature Fisher-Tropsch process. The temperature range may be between 250°C and 400°C, typically from 300°C to 370°C, and even from 330°C to 350°C. The pressure may be from 10 to 60 bar (1 to 6 MPa), typically from 15 to 30 bar, and usually at about 20 bar.

20 The at least one carbon oxide in the syngas preferably comprises CO. The carbon oxide may comprise a mixture of CO and CO<sub>2</sub>.

The reaction may be carried out in any suitable reactor. It is foreseen that it will be carried out in a fluidised bed reactor, preferably in a fixed fluidised bed.

ART 3A AMDT

## 6

reactor. If the CO hydrogenation (hydrocarbon synthesis) catalyst and the acidic catalyst are contained on separate particles, the invention is especially suited to a fluidised bed reactor, since there will not be extensive direct contact between the different catalysts which will reduce migration of the alkali promoters from the hydrocarbon synthesis catalyst to the acidic catalyst, thereby reducing the detrimental results associated with such migration.

The hydrocarbon synthesis catalyst may comprise any suitable alkali-promoted iron catalyst suitable for CO hydrogenation but preferably it comprises a Fischer-Tropsch catalyst. The iron catalyst preferably comprises a precipitated iron catalyst, but it may also comprise a fused iron catalyst. If the process is to be performed in a fluidised bed reactor, the final catalyst may be produced by means of a variety of known methods in order to obtain particles with acceptable fluidisation properties, such as crushing, spray-drying, etc. In order to obtain a particle size distribution suitable for fluidisation, the catalyst may be classified by means of known methods, such as sieving, cyclone classification, etc.

The iron catalyst contains at least one alkali promoter usually in the form of an alkali oxide. The alkali promoter preferably comprises potassium or sodium oxide. The catalyst may contain more than one alkali promoter. The alkali can be added to the iron by means various methods, such as impregnation of the iron with the alkali, co-precipitating the alkali with the iron, fusing the iron and the alkali, etc. The total alkali metal content (mol alkali metal per 100 g iron) must preferably

ART 34 AMDT

15

feed to the reactor was rich in hydrogen and the alkali metal content of the iron catalyst was low. The C<sub>5</sub><sup>+</sup> selectivity was about 50% for both examples of the process according to the invention.

5 It is further clear that the addition of an acidic catalyst to the Fischer-Tropsch process increased the selectivity of the condensable hydrocarbons. The selectivity of the C<sub>5</sub><sup>+</sup> hydrocarbons increased significantly, especially in the case of the "low alumina content" HZSM-5. The increase in the C<sub>5</sub> to C<sub>11</sub> fraction, which contains most of the gasoline range components, was even more substantial.

The results also indicate that the normal Fischer-Tropsch product consists mainly of linear hydrocarbons and contains little aromatic and branched compounds. Since linear hydrocarbons have a very low octane value, they are undesirable as gasoline components. By adding an acid catalyst to the process, the amount of aromatics in the product increased dramatically and the paraffins and olefins became substantially more branched. These effects are especially noted for the case of the "high alumina content" HZSM-5.

20 The examples presented therefore clearly illustrate that the addition of an acidic catalyst to the Fischer-Tropsch process not only increases the selectivity of compounds that fall inside the gasoline range, but also that an improved gasoline fraction, containing substantially higher amounts of high octane value compounds such as aromatics, branched paraffins and branched olefins, is

ART 3A AMDT

produced.

### Examples B

5

The additional examples are intended to demonstrate that the requirement that the C<sub>5+</sub> hydrocarbon fraction of at least 30 mass % is satisfied at the extremes of the alkali metal content range (0.005 to 0.01 mol alkali metal/100g Fe). It is also intended to demonstrate that this requirement is also satisfied at high hydrogen to carbon oxide ratios in the syngas.

### Catalysts

15

Precipitated iron catalysts containing varying levels of alkali were employed as the syngas conversion catalyst. The catalysts were prepared by reverse precipitation. For each preparation approximately 170 ml 25% aqueous ammonium hydroxide (NH<sub>4</sub>OH) solution was added to 400 ml of an 1 M aqueous solution of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) while stirring. Precipitation was allowed to occur until a pH of 7. A 0.005 M potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) or sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution was added to the precipitate in appropriate amounts to achieve the desired concentration of promoter in each catalyst. The precipitate was dried at 130°C overnight, and calcined at 350°C for four hours. The compositions of the catalysts are presented in Table 4.

25

PART 3A AMDT

20

**Table 6: The Influence of alkali metal level and hydrogen/carbon oxide ratio on the selectivity for C<sub>5</sub>+ (mass %)**

Catalyst No.	Alkali	Alkali metal Concentration (mol/100g Fe)	Run no.	H <sub>2</sub> /CO+CO <sub>2</sub> ) ratio	C <sub>5</sub> + selectivity (mass %)
PS01	K	0.0045	1	2.7	41
			2	4.5	32
PS02	Na	0.0045	3	2.7	43
			4	4.5	35
			5	5.8	30
PS03	K	0.009	6	2.6	53
			7	4.4	46
			8	4.9	41
PS04	Na	0.009	9	2.6	56
			10	4.4	49
			11	5.0	45

- 5 It is clear that at alkali metal levels between 0.0045 and 0.009 mol alkali metal/100 g Fe, and at hydrogen to carbon oxide feed ratios of up to 5 or more the requirement of >30 % C<sub>5</sub>+ selectivity is satisfied.

10

ATT 3A SHEET

21

CLAIMS

1. A hydrocarbon synthesis process comprising the conversion of a feed of H<sub>2</sub> and at least one carbon oxide to hydrocarbons containing at least 30% on a mass basis hydrocarbons with five or more carbon atoms (hereinafter referred to as C<sub>5+</sub> compounds); the conversion being carried out in the presence of an alkali metal promoted iron hydrocarbon synthesis catalyst and an acidic catalyst suitable for converting hydrocarbons; and the process being characterised therein that the reaction mixture formed during the conversion contains less than 0.02 mol alkali metal per 100g iron and that the H<sub>2</sub> : carbon oxide molar ratio in the feed of H<sub>2</sub> and carbon oxide is at least 2.
2. The process of claim 1 wherein the synthesised hydrocarbons contain at least 40% on a mass basis C<sub>5+</sub> compounds.
3. The process of either one of claims 1 or 2 wherein the hydrocarbon synthesis process comprises a high temperature Fischer-Tropsch process.
4. The process of any one of the preceding claims wherein the at least one carbon oxide in the syngas comprises CO.
5. The process of claim 3 wherein the alkali-metal promoted iron hydrocarbon

ART 34 AMDT

synthesis catalyst comprises a Fisher-Tropsch catalyst.

6. The process of claim 5 wherein the promoter comprises potassium or sodium oxide.
7. The process of any one of the preceding claims wherein the acidic catalyst comprises a zeolite.
10. 8. The process of claim 7 wherein the zeolite comprises a HZSM-5 zeolite.
9. The process of any one of the preceding claims wherein the hydrocarbon synthesis catalyst and the acidic catalyst are contained on separate particles.
15. 10. Hydrocarbons produced by the process of any one of claims 1 to 9.
11. The use of a hydrocarbon synthesis process for the conversion of a feed of H<sub>2</sub> and at least one carbon oxide to hydrocarbons containing at least 30% on a mass basis hydrocarbons with five or more carbon atoms (hereinafter referred to as C<sub>5+</sub> compounds), the process comprising converting a feed of H<sub>2</sub> and at least one carbon oxide to hydrocarbons in the presence of an alkali promoted iron hydrocarbon synthesis catalyst and an acidic catalyst suitable for converting hydrocarbons; and the

ART 34 AMDT

23

process being characterise therein that the reaction mixture formed during the conversion contains less than 0.02 mol alkali metal per 100g iron and that the H<sub>2</sub> : carbon oxide molar ratio in the feed of H<sub>2</sub> and carbon oxide is at least 2.

5

10

15

20

a heavier hydrocarbon product despite the low alkali level. It is well-known that a high H<sub>2</sub> : CO ratio in the feed favours products which are not desirable for gasoline production. Accordingly if a low level of alkali promoter is considered a relatively low H<sub>2</sub>: CO ratio in the feed will be considered to avoid production of 5 excessively light hydrocarbons.

Surprisingly it has now been found that if hydrocarbon synthesis of syngas is carried out in the presence of a hydrocarbon synthesis catalyst and an acid catalyst under conditions where:

- 10 i) the hydrocarbon synthesis catalyst includes a low level of alkali; and  
ii) the hydrogen to carbon monoxide ratio of the syngas feed stream is relatively high,

a hydrocarbon product is produced that is suitable for use as gasoline. This is true even if the synthesis is carried out under high temperature Fischer-Tropsch 15 conditions.

#### Disclosure of the Invention

According to the present invention there is provided a hydrocarbon synthesis 20 process comprising the conversion of a feed of H<sub>2</sub> and at least one carbon oxide to hydrocarbons containing at least 30% on a mass basis hydrocarbons with five or more carbon atoms (hereinafter referred to as C<sub>5+</sub> compounds), the conversion being carried out in the presence of an alkali-promoted iron hydrocarbon synthesis catalyst and an acidic catalyst suitable for converting

hydrocarbons; and the process being characterised therein that the reaction mixture formed during the conversion contains less than 0.02 mol alkali per 100g iron and that the H<sub>2</sub> : carbon oxide molar ratio in the feed of H<sub>2</sub> and carbon oxide is at least 2.

5

The synthesised hydrocarbons preferably contain, on a mass basis, at least 35%, more preferably at least 40% and most preferably at least 50%, C<sub>5</sub><sup>+</sup> compounds. Preferably, the process is for producing liquid fuel, especially gasoline and preferably unleaded gasoline. The process may also be used for

10 producing hydrocarbons rich in aromatics such as benzene, toluene and xylenes and/or hydrocarbons rich in branched hydrocarbons and/or rich in olefins.

The hydrocarbon synthesis process may comprise a Fischer-Tropsch process,

15 preferably a high temperature Fisher-Tropsch process. The temperature range may be between 250°C and 400°C, typically from 300°C to 370°C, and even from 330°C to 350°C. The pressure may be from 10 to 60 bar (1 to 6 MPa), typically from 15 to 30 bar, and usually at about 20 bar.

20 The at least one carbon oxide in the syngas preferably comprises CO. The carbon oxide may comprise a mixture of CO and CO<sub>2</sub>.

The reaction may be carried out in any suitable reactor. It is foreseen that it will be carried out in a fluidised bed reactor, preferably in a fixed fluidised bed

reactor. If the CO hydrogenation (hydrocarbon synthesis) catalyst and the acidic catalyst are contained on separate particles, the invention is especially suited to a fluidised bed reactor, since there will not be extensive direct contact between the different catalysts which will reduce migration of the alkali promoters from 5 the hydrocarbon synthesis catalyst to the acidic catalyst, thereby reducing the detrimental results associated with such migration.

The hydrocarbon synthesis catalyst may comprise any suitable alkali-promoted iron catalyst suitable for CO hydrogenation but preferably it comprises a 10 Fischer-Tropsch catalyst. The iron catalyst preferably comprises a precipitated iron catalyst, but it may also comprise a fused iron catalyst. If the process is to be performed in a fluidised bed reactor, the final catalyst may be produced by means of a variety of known methods in order to obtain particles with acceptable fluidisation properties, such as crushing, spray-drying, etc. In order 15 to obtain a particle size distribution suitable for fluidisation, the catalyst may be classified by means of known methods, such as sieving, cyclone classification, etc.

The iron catalyst contains at least one alkali promoter usually in the form of an 20 alkali oxide. The alkali promoter preferably comprises potassium or sodium oxide. The catalyst may contain more than one alkali promoter. The alkali can be added to the iron by means various methods, such as impregnation of the iron with the alkali, co-precipitating the alkali with the iron, fusing the iron and the alkali, etc. The total alkali content (mol alkali per 100 g iron) must preferably

feed to the reactor was rich in hydrogen and the alkali content of the iron catalyst was low. The C<sub>5</sub><sup>+</sup> selectivity was about 50 % for both examples of the process according to the invention.

- 5 It is further clear that the addition of an acidic catalyst to the Fischer-Tropsch process increased the selectivity of the condensable hydrocarbons. The selectivity of the C<sub>5</sub><sup>+</sup> hydrocarbons increased significantly, especially in the case of the "low alumina content" HZSM-5. The increase in the C<sub>5</sub> to C<sub>11</sub> fraction, which contains most of the gasoline range components, was even more
- 10 substantial.

The results also indicate that the normal Fischer-Tropsch product consists mainly of linear hydrocarbons and contains little aromatic and branched compounds. Since linear hydrocarbons have a very low octane value, they are

15 undesirable as gasoline components. By adding an acid catalyst to the process, the amount of aromatics in the product increased dramatically and the paraffins and olefins became substantially more branched. These effects are especially noted for the case of the "high alumina content" HZSM-5.

- 20 The examples presented therefore clearly illustrate that the addition of an acidic catalyst to the Fischer-Trospch process not only increases the selectivity of compounds that fall inside the gasoline range, but also that an improved gasoline fraction, containing substantially higher amounts of high octane value compounds such as aromatics, branched paraffins and branched olefins, is

produced.

**Examples B**

5

The additional examples are intended to demonstrate that the requirement that the C<sub>5</sub>+ hydrocarbon fraction of at least 30 mass % is satisfied at the extremes of the alkali content range (0.005 to 0.01 mol alkali/100g Fe). It is also intended to demonstrate that this requirement is also satisfied at high hydrogen to carbon

10 oxide ratios in the syngas.

**Catalysts**

15 Precipitated iron catalysts containing varying levels of alkali were employed as the syngas conversion catalyst. The catalysts were prepared by reverse precipitation. For each preparation approximately 170 ml 25% aqueous ammonium hydroxide (NH<sub>4</sub>OH) solution was added to 400 ml of an 1 M aqueous solution of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) while stirring. Precipitation  
20 was allowed to occur until a pH of 7. A 0.005 M potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) or sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution was added to the precipitate in appropriate amounts to achieve the desired concentration of promoter in each catalyst. The precipitate was dried at 130°C overnight, and calcined at 350°C for four hours. The compositions of the catalysts are presented in Table 4.

25

Table 6: The influence of alkali level and hydrogen/carbon oxide ratio on the selectivity for C<sub>5</sub>+ (mass %)

Catalyst No.	Alkali	Alkali concentration (mol/100g Fe)	Run no.	H <sub>2</sub> /(CO+CO <sub>2</sub> ) ratio	C <sub>5</sub> + selectivity (mass %)
PS01	K	0.0045	1	2.7	41
			2	4.5	32
PS02	Na	0.0045	3	2.7	43
			4	4.5	35
			5	5.8	30
PS03	K	0.009	6	2.6	53
			7	4.4	46
			8	4.9	41
PS04	Na	0.009	9	2.6	56
			10	4.4	49
			11	5.0	45

- 5 It is clear that at alkali levels between 0.0045 and 0.009 mol alkali/100 g Fe, and at hydrogen to carbon oxide feed ratios of up to 5 or more the requirement of >30 % C<sub>5</sub>+ selectivity is satisfied.

CLAIMS

1. A hydrocarbon synthesis process comprising the conversion of a feed of  
5      H<sub>2</sub> and at least one carbon oxide to hydrocarbons containing at least 30%  
on a mass basis hydrocarbons with five or more carbon atoms (hereinafter  
referred to as C<sub>5+</sub> compounds); the conversion being carried out in the  
presence of an alkali-promoted iron hydrocarbon synthesis catalyst and an  
acidic catalyst suitable for converting hydrocarbons; and the process being  
10     characterised therein that the reaction mixture formed during the  
conversion contains less than 0.02 mol alkali per 100g iron and that the  
H<sub>2</sub> : carbon oxide molar ratio in the feed of H<sub>2</sub> and carbon oxide is at least  
2.
- 15     2. The process of claim 1 wherein the synthesised hydrocarbons contain at  
least 40% on a mass basis C<sub>5+</sub> compounds.
- 20     3. The process of either one of claims 1 or 2 wherein the hydrocarbon  
synthesis process comprises a high temperature Fischer-Tropsch process.
4. The process of any one of the preceding claims wherein the at least one  
carbon oxide in the syngas comprises CO.
5. The process of claim 3 wherein the alkali-promoted iron hydrocarbon

synthesis catalyst comprises a Fisher-Tropsch catalyst.

6. The process of claim 5 wherein the promoter comprises potassium or sodium oxide.

5

7. The process of any one of the preceding claims wherein the acidic catalyst comprises a zeolite.

8. The process of claim 7 wherein the zeolite comprises a HZSM-5 zeolite.

10

9. The process of any one of the preceding claims wherein the hydrocarbon synthesis catalyst and the acidic catalyst are contained on separate particles.

15 10. Hydrocarbons produced by the process of any one of claims 1 to 9.